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(54) Title: LOW-EMISSIONS DIESEL FUEL EMULSIONS

(57) Abstract: A low-emissions diesel fuel comprises fungible aviation kerosene emulsified with from 1 to 30 % water, and preferably contains 50-300 ppm detergent and 25-500 ppm lubricity additive. Improved results can be achieved by also employing a fuel-soluble platinium group compound, such as 0.1-2.0 ppm platinium COD and a fuel-soluble cerium compound, such as 5-20 ppm cerium oleate. A method of reducing the emissions of pollutants from a diesel engine, comprising running the engine on a fuel as defined. The method is improved by also employing another pollution-reducing technique selected from timing changes, exhaust gas recirculation, oxidation catalysts, lean NO_x catalysts and particulate filters for enhanced emissions control,

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LOW-EMISSIONS DIESEL FUEL EMULSIONS

Background Of The Invention

The invention concerns a new low-emissions diesel fuel based on an emulsion of a base fuel designed for use in jet engines and modified for use in diesel engines, especially of the type used to power buses in metropolitan areas where emissions are of special concern.

Efforts are being made in many jurisdictions to reduce the emissions of regulated pollutants like carbon monoxide, nitrogen oxides (NO_x) and particulates. The technologies have included those that modify the combustion conditions and fuels, known as primary measures, and those that treat the exhaust after combustion, known as secondary measures. When effective primary measures are employed, the secondary measures can still be employed to achieve further reductions.

There is a need for a new low-emissions fuel for use in diesel engines to reduce emissions of one or more regulated pollutants.

Summary Of The Invention

The invention provides a new low-emissions fuel for use in diesel engines and a method of reducing pollutant emissions from diesel engines. The diesel fuel of the invention is in the form of an emulsion and its formulation and use in diesel engines are described below.

Many of the preferred aspects of the invention are described below. Equivalent compositions are contemplated.

Description Of The Invention

The invention provides a new diesel fuel comprised of an emulsion of water and a base fuel comprising a lubricity additive and a detergent. It is surprising that although a platinum and/or cerium fuel additive can be employed, such is not essential to the achievement of surprisingly good emission reductions as compared to conventional diesel fuel and diesel fuel emulsions.

The preferred detergent comprises polyolefin amide alkyleneamine (about 65-80%) and the remainder petroleum distillate. Equivalents which have the same essential function can also be employed. One preferred form is available from Texaco as TFA-4690-C, at concentrations of from about 50 to 300 ppm, more narrowly 75 to 150 ppm, e.g., about 100ppm, for which they provide the following analysis:

Properties	Method	Typical
Density @ 15°C	D4052	0.91-0.94
Nitrogen Content, wt.%	D5291	2.3-2.4
Flash, °C, minimum	D93	62
TBN, mgKOH/g	D2896	50-60
Kinematic Viscosity, cSt at 40°C	D445	600-850

A preferred lubricity additive comprises tall oil fatty acids, available commercially as mixture of fatty acids including oleic, linoleic and the like. Equivalents which have the same essential function can also be employed.

Dimer acids are high molecular weight dibasic acids produced by the dimerization of unsaturated fatty acids at mid-molecule and usually contain 21-36 carbons. Similarly, trimer acids contain three carboxyl groups and usually 54 carbons. Dimer and trimer acids are generally made by a Diels Alder reaction. This usually involves the reaction of an unsaturated fatty acid with another polyunsaturated fatty acid--typically linoleic acid. Starting raw materials usually include tall oil fatty acids. In addition, it is also known to form dimer and trimer acids by reacting acrylic acid with polyunsaturated fatty acids.

After the reaction, the product usually comprises a small amount of monomer units, dimer acid, trimer acid, and higher analogs. Where the product desired is primarily dimer acid (i.e., at least about 85% dimer acid), the reactant product is often merely referred to as dimer acid. However, the individual components can be separated to provide a more pure form of dimer acid or trimer acid by itself. Suitable dimer acids for use in this invention include Westvaco Diacid 1550, commercially available from Westvaco Chemicals of Charleston Heights, S.C.; Unidyme 12 and Unidyme 14, commercially available from Union Camp Corporation of Dover, Ohio; Empol 1022, commercially available from Henkel Corporation of Cincinnati, Ohio; and Hystrene 3695, commercially available from Witco Co. of Memphis, Tenn.

In addition, blends of dimer and trimer acids can also be used as the lubricity additive of the present invention. These blends can be formed by combining dimer and trimer acids, or can comprise the reaction product from the formation of the dimer acid, which can contain substantial amounts of trimer acid. Generally, blends comprise about 5% to about 80% dimer acid. Specific blends include a blend of about 75% dimer acid and about 25% trimer acid, commercially available as Hystrene 3675, a blend of 40% dimer acid and 60% trimer acid, commercially available as Hystrene 5460, and a blend of about 60% dimer acid and about 40% trimer acid, all commercially available from Witco Co. of Memphis, Tenn.

One preferred form of lubricity additive is available from Texaco as TFA-4769, at concentrations of from about 25 to 500 ppm, e.g., about 50-150 ppm, for which they provide the following analysis:

Properties	Method	Typical
Specific Gravity, 60/60°F	D1298	0.91
Pounds/Gallon, 60°F	Calculated	7.54
Flash, °F, minimum	D93	142
Kinematic Viscosity, cSt at 40°C	D445	17.85

The base fuel comprises a commercially-available jet fuel. It can be purchased from Colonial Pipeline Company as "fungible aviation kerosene grade 55". Equivalents which have the same essential function and those varying compositionally by up to 15 %, preferably by less than 5%, can also be employed. It is characterized by the following average analysis:

	ASTM Test	
Parameter	Method	Value
Cetane Number	D-613	50.4
Hdrocarbon	D-1319	
Aromatics, vol%		15.3
Olefins, vol%		1.8
Saturates, vol%		82.9
Flash Point (°F)	D-93	138
API Gravity	D-4052	44.4
Specific Gravity		0.8045
Viscosity, 40°C (cSt)	D-445	1.46
Sulfur (weight %)	D-2622	0.0334[1]
ppm		334
Heat of Combustion,		
Gross (BTU/Pound)	D-240	19,794.7
Net (BTU/Pound)		18,519.4
Pour Point (°C)	D-97	-48
Cloud Point (°C)	D-2500	-45
Cetane Index (calculated)	D-976	42 minimum, 48 test

[1] Lower sulfur forms of this formulation, as low as 5 to 30 ppm sulfur, can provide further advantages and are included.

Simulated Distillation (°C)	D-2887
IBP	119.7
5	156.7
10	167.2
15	173.8
20	180.8
30	194.3
40	203.6
50	215.3
60	226.2
70	235.7
80	250.2
90	265.1
95	276.3
FBP	304.7

The fuel as described above will be formulated as an emulsion of water-in-oil where the emulsion is made by inclusion of from 1 to 30% of an aqueous phase with 70-99% of the oil phase as previously defined. Surfactants, lubricity agents and/or corrosion inhibitors can be added as described in U. S. Patent No. 5,743,922 or as otherwise known in the art. An emulsion of water-in-oil typically provides about 1% NO_x reduction for each 1% water added. The new fuel improves the reductions in pollutants normally achieved with diesel fuel emulsions and its combination with other pollution control technologies will provide emissions reductions greater than either alone. The use of platinum group metal and/or cerium fuel-borne catalysts is optional, but can further enhance reductions. In one preferred form, the emulsion is prepared in the absence of such additives.

The fuel thus formed can be used to fuel a diesel engine with reduced emissions of pollutants, which can be further enhanced with the simultaneous use of

engine timing changes, exhaust gas recirculation, oxidation catalysts, lean NO_x catalysts and/or particulate filters for enhanced emissions control.

The fuel can contain a fuel-soluble catalyst comprised of fuel-soluble platinum group metal compositions and/or cerium compositions. One or more of these optional additives can be employed in forms and amounts effective to deliver the catalytic metal in active form to the exhaust system of a diesel engine.

Among the specific cerium compounds are: cerium III acetylacetonate, cerium III napthenate, and cerium octoate and other soaps such as stearate, neodecanoate, and octoate (2-ethylhexoate). Many of the cerium compounds are trivalent compounds meeting the formula: Ce $(OOCR)_3$ wherein R=hydrocarbon, preferably C_2 to C_{22}, and including aliphatic, alicyclic, aryl and alkylaryl. The cerium is preferred at concentrations of 2 to 20 ppm, more narrowly form 4 to 15 ppm, cerium w/v of fuel, *i.e.*, weight of cerium metal in mg to volume of fuel in liters. Preferably, the cerium is supplied as cerium hydroxy oleate propionate complex (40% cerium by weight). Preferred levels are toward the lower end of this range.

Any of the platinum group metal compositions, e.g., 1,5-cyclooctadiene platinum diphenyl (platinum COD), described in U.S. Pat. No. 4,891,050 to Bowers, et al., U.S. Pat. No. 5,034,020 to Epperly, et al., and U.S. Pat. No. 5,266,093 to Peter-Hoblyn, et al., can be employed as the platinum source. Other suitable platinum group metal catalyst compositions include commercially-available or easily-synthesized platinum group metal acetylacetonates, platinum group metal dibenzylidene acetonates, and fatty acid soaps of tetramine platinum metal complexes, e.g., tetramine platinum oleate. The platinum is preferred at concentrations of 0.1 – 2.0 ppm, *e.g.*, up to about 1.0 ppm platinum w/v of fuel. Preferred levels are toward the lower end of this range, e.g., 0.15 –0.5 ppm. Platinum COD is the preferred form of platinum for addition to the fuel.

The term "diesel particulate filter" is meant to refer to those devices known in the art as exhaust gas filters that reduce particulate emissions by trapping a portion of the particulates within a complex internal structure. They must be regenerated or

replaced as deposits will accumulate. The fuel borne catalyst described above, when used with the base fuel as also described – forming the fuel of the invention – enables very reduced emissions with enhanced filter operation.

The term "lean NO_x catalysts" is meant to refer to those devices known in the art for catalytically reducing NO_x emissions under lean fuel (oxygen-rich) conditions. Suitable catalysts of this type are described in U. S. Patent No. 4,904,633 to Ohata , *et al.*, which is hereby incorporated by reference in its entirety.

The term "diesel oxidation catalyst" is meant to refer to those devices known in the art as exhaust gas treatment catalysts that reduce particulate, hydrocarbon and carbon monoxide emissions by causing contact with catalyzed surfaces in lieu of trapping particulates as done in the diesel particulate filters. The fuel borne catalyst described above, when used with the base fuel as also described – forming the fuel of the invention – enables very reduced emissions with enhanced oxidation catalyst operation.

Retarding engine timing, *e.g.,* by from about 2 to about 6°, is a known procedure for reducing NO_x, unfortunately it will by itself cause pollutant generation due to poor combustion. This tradeoff has been troubling the art since emissions control became important. It is an advantage of the invention, that both reduced NO_x and other pollutants can be achieved by employing the fuel of the invention in combination with one or more of the above techniques and/or exhaust gas recirculation wherein a portion of the exhaust gas is intermixed with combustion air.

The following Examples are provided to further illustrate and explain a preferred form of the invention and are not to be taken as limiting in any regard. Unless otherwise indicated, all parts and percentages are by weight.

Example 1

This example describes the preparation of a low-emissions diesel fuel according to a preferred aspect of the invention. A fuel is blended using the Colonial

Pipeline Company fungible aviation kerosene grade 55 analyzed above, with 100 ppm of the TFA 4690-C detergent, 150-250 ppm of the noted Texaco lubricity additive and 20% water by weight. The fuel was emulsified to obtain a water in oil emulsion which is used to fuel a diesel engine with reduced production of pollutants.

The above description is intended to enable the person skilled in the art to practice the invention. It is not intended to detail all of the possible modifications and variations which will become apparent to the skilled worker upon reading the description. It is intended, however, that all such modifications and variations be included within the scope of the invention which is seen in the above description and otherwise defined by the following claims. The claims are meant to cover the indicated elements and steps in any arrangement or sequence which is effective to meet the objectives intended for the invention, unless the context specifically indicates the contrary.

CLAIMS

1. A low-emissions diesel fuel comprising an emulsion of from 1 to 30% of an aqueous phase and 70-99% of an oil phase comprised of aviation grade kerosene, detergent and lubricity additive.

2. A low-emissions diesel fuel according to claim 1 formulated as an emulsion of water-in-oil where and contains 50-300 ppm detergent, 25-500 ppm lubricity additive.

3. A low-emissions diesel fuel according to claim 1 formulated as an emulsion of water-in-oil where and contains aviation kerosene grade 55.

4. A low-emissions fuel according to claim 1, further comprising platinum and/or cerium fuel additives.

5. A low-emissions diesel fuel according to claim 4 comprising fuel-soluble platinum composition and fuel-soluble cerium composition.

6. A low-emissions diesel fuel formulated as an emulsion of water-in-oil where the emulsion is made by inclusion of from 1 to 30% of an aqueous phase with 70-99% of an oil phase comprising fungible aviation kerosene grade 55, 50-300 ppm detergent, 150-250 ppm lubricity additive and 0.1 –1.0 ppm platinum supplied as platinum COD and 2-15 ppm cerium supplied as cerium hydroxy oleate propionate complex.

7. A method of reducing the emissions of pollutants from a diesel engine, comprising running the engine on a fuel as defined in any of claims 1-7.

8. A method of reducing the emissions of pollutants from a diesel engine according to claim 7 wherein the method is improved by also employing another pollution-reducing technique selected from timing changes, exhaust gas recirculation, oxidation catalysts, lean NO_x catalysts and particulate filters for enhanced emissions control.

9. A method of reducing the emissions of pollutants from a diesel engine, comprising running the engine on a fuel formulated as an emulsion of water-in-oil where the emulsion is made by inclusion of from 1 to 30% of an aqueous phase with 70-99% of an oil phase comprising fungible aviation kerosene grade 55, 50-300 ppm detergent, 150-250 ppm lubricity additive fuel-soluble platinum composition and fuel-soluble cerium composition, and also including also employing another pollution-reducing technique selected from timing changes, exhaust gas recirculation, oxidation catalysts, lean NO_x catalysts and particulate filters for enhanced emissions control.

10. A method of reducing the emissions of pollutants from a diesel engine according to claim 9 which contains 0.1 – 2.0 ppm platinum supplied as platinum COD and 2 - 15 ppm cerium supplied as cerium hydroxy oleate propionate complex

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US01/30606

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :C10L 1/00, 1/32
US CL :44/301,354,357

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 44/301,354,357

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,693,106 A (PETER-HOBLYN et al) 02 December 1997, see col. 4, lines 28-37, 59; col. 5, lines 21-25, 53-59; col. 6, lines 1-3, 10-19; col. 10, lines 31-42.	1-5,7-9
Y	US 5,584,894 A (PETER-HOBLYN et al) 17 December 1996, see col. 3, lines 43-51, 60-64 col. 4, lines 10-18; col. 6, lines 48-67; col. 11, lines 50-61.	1-10
Y	US 5,284,492 A (DUBIN) 08 February 1994, see col. 4, lines 1-4, 11-15; col. 7, lines 66-68.	1-10
Y	US 4,696,638 A (DENHERDER) 29 September 1987, see abstract; col. 4, lines 20-29; col. 3, lines 5-11	1-10

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
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